

# **Low Temperature Sintering of BZT-BCT Using Alkalifree Glass Additives and its Dielectric Property**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT  
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**In**

**Ceramic Engineering**

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## CERTIFICATE

This is to certify that the thesis entitled, "**Low Temperature sintering of BZT-BCT using alkalifree glass additive and its dielectric property** " submitted by **Shammee Bansal** in partial fulfillment of the requirement for the award of **Bachelor of Technology Degree in Ceramic Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date:

Prof. Ranabrata Mazumder  
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## Content

Chapter 1	Introduction	1-5
Chapter 2	Literature Survey	6- 12
2.1	Objective	12
Chapter 3	Experimental Work	13-17
3.1	Preparation of BZT-BCT Powders	14
3.2	Preparation of $\text{SrB}_4\text{O}_7$ glass	15
3.3	Preparation of $\text{BaO}.\text{SiO}_2.\text{B}_2\text{O}_3$ glass	16
3.4	Characterization	18
3.4.1	Phase and microstructure analysis	18
3.4.2	Density Measurement	18
3.4.3	Dielectric Measurement	18
Chapter 4	Result and Discussion	19-31
4.1	Densification of BZT-BCT with $\text{SrB}_4\text{O}_7$ glass	19
4.2	XRD analysis of $\text{SrB}_4\text{O}_7$	21
4.3	Densification of BZT-BCT with $\text{BaO},\text{SiO}_2, \text{B}_2\text{O}_3$ glass	22
4.4	Phase analysis of $\text{BaO}, \text{SiO}_2, \text{B}_2\text{O}_3$ glass and glass added sintered BZT-BCT ceramics	25
4.5	Dielectric Properties	28
4.6	Microstructural analysis	30
Chapter 5	Conclusions and References	32-35
5.1	Conclusions	33
5.2	References	34

## **Abstract**

Low temperature sintering of  $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3 - 0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  [BZT-BCT] was studied using two different glass additive namely, strontium borate ( $\text{SrB}_4\text{O}_7$ ) and  $\text{BaO}, \text{SiO}_2, \text{B}_2\text{O}_3$ . First, single phase BZT–BCT powders were prepared by conventional solid state reaction technique at  $1200^\circ\text{C}$ . It was observed that strontium borate is not an effective sintering additive for BZT–BCT. BZT–BCT can be successfully sintered to more than 94% of theoretical density at  $1150^\circ\text{C}$  with  $\text{BaO}, \text{SiO}_2, \text{B}_2\text{O}_3$  glass additive, whereas the conventional sintering temperature is around  $1400^\circ\text{C}$ . The relative permittivity of such low-temperature sintered samples was reduced compared to BZT-BCT samples prepared via conventional sintering at a high temperature. It is also found that the addition of  $\text{BaO}, \text{SiO}_2, \text{B}_2\text{O}_3$  glass additive promotes grain growth.

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## List of figures

Fig 1: Schematic Representation of Perovskite structure ( $ABO_3$ ).

Fig 2: Phase diagram of pseudo-binary ferroelectric system  $\{xBa(Zr_{0.2}Ti_{0.8})O_3\}-\{(1-x)(Ba_{0.7}Ca_{0.3})TiO_3\}$ .

Fig 3: Flow chart for Preparation of BZT-BCT powders.

Fig 4: Flow Chart for the preparation of  $SrB_4O_7$  glass powder.

Fig 5: Flow Chart for the preparation of  $SrB_4O_7$  glass added BZT-BCT ceramic.

Fig 6: Flow Chart for the preparation of  $BaO.SiO_2.B_2O_3$  glass powder.

Fig 7: Flow Chart for the preparation of  $BaO.SiO_2.B_2O_3$  glass added BZT-BCT Ceramic.

Fig 8: XRD analysis of  $SrB_4O_7$  glass.

Fig 9: X-ray diffraction patterns of the modified BZT-BCT glass ceramics sintered at  $1000^\circ\text{C}$  for 2h.

Fig 10: Bulk Density of  $BaO-SiO_2-B_2O_3$  glass added BZT-BCT ceramics.

Fig 11: XRD analysis of  $BaO-SiO_2-B_2O_3$  glass

Fig 12(a): X-ray diffraction patterns of the glass added BZT-BCT ceramics sintered at  $1100^\circ\text{C}$  for 1hrs.

Fig 12(b): X-ray diffraction patterns of the glass added BZT-BCT ceramics sintered at  $1150^\circ\text{C}$  for 1hrs.

Fig 13: (a) Room temperature relative permittivity ( $\epsilon_r$ ) of glass added BZT-BCT ceramics sintered at  $1100^\circ\text{C}$  for 2 hrs.

Fig 13: (b) Room temperature loss factor ( $\tan\delta$ ) of glass added BZT-BCT ceramics sintered at  $1100^\circ\text{C}$  for 2 hrs.

Fig 14: (a) Room temperature relative permittivity ( $\epsilon_r$ ) of glass added BZT-BCT ceramics sintered at  $1150^\circ\text{C}$  for 1 hrs.

Fig 14: (b) Room temperature dissipation factor ( $\tan\delta$ ) of glass added BZT-BCT ceramics sintered at  $1150^\circ\text{C}$  for 1 hrs.

Fig 15: FESEM micrograph of as fired surface and fracture of 10 wt%  $BaO-SiO_2-B_2O_3$  added BZT-BCT ceramics (a) -(b)  $1100^\circ\text{C}/1\text{h}$  (c)-(d)  $1100^\circ\text{C}/2\text{h}$  (e)  $1150^\circ\text{C}/1\text{h}$

## List of Tables

Table 1: Density of  $SrB_4O_7$  added BZT-BCT glass ceramics.

Table 2: Bulk Density of  $BaO-SiO_2-B_2O_3$  glass added BZT-BCT ceramics.

# **Chapter 1**

## **Introduction**

## 1. INTRODUCTION

Barium titanate ( $\text{BaTiO}_3$ )-based ceramics, due to their outstanding dielectric and ferroelectric properties, are used in the electronic industry for the application in thermistors, multilayer ceramic capacitors (MLCC), memory materials, transducers, actuators, sensor, high-k dielectrics and dynamic random access memory [1,2]. The high energy storage materials which can increase the efficiency of electric power system required large dielectric permittivity and high electrical breakdown strength are two essential factors to attain high energy density. Low dielectric loss, fast charge and discharge speed, and cheap cost are also important factors for energy storage applications [2].

$\text{BaTiO}_3$  is isostructural with the mineral perovskite ( $\text{CaTiO}_3$ ) and so is referred to as ‘a perovskite’. In perovskite structure,  $\text{ABO}_3$  where ‘A’ and ‘B’ are cation elements or mixture of two or more cation elements. In the ideal perovskite crystal structure shown in Fig 1, if ‘A’ atom is taken at the corner of the cube, then ‘B’ atom resides in the body centre and an oxygen atom at each face Centre of the cube.

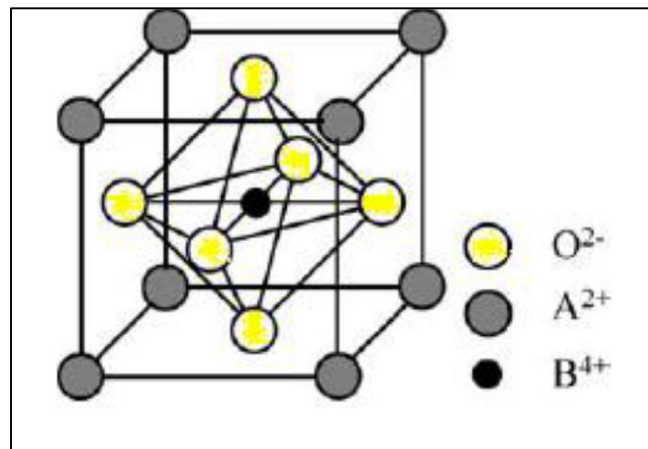


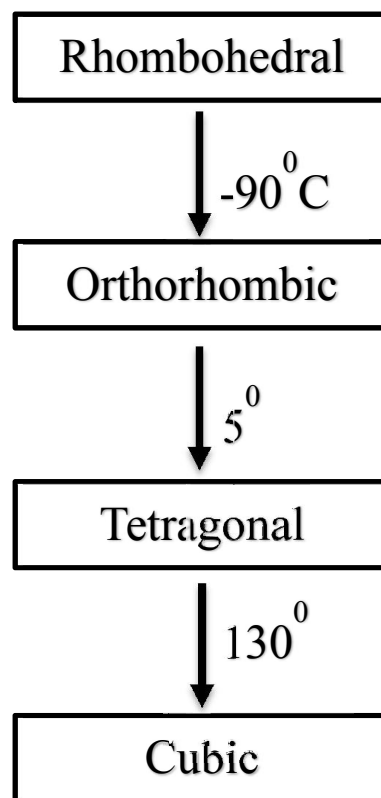
Fig 1: Schematic Representation of Perovskite structure ( $\text{ABO}_3$ )



The perovskite structure permits wide modifications by the isovalent or aliovalent substituent at A or B sites with cations of approximately matching ionic radii. Barium Titanate ceramics show remarkable variation in their physical and structural characteristics with respect to ‘Ca’ and ‘Zr’ substitution [1].

## 1.1 Modification of Barium Titanate

Owing to the high relative permittivity and easy manufacturing process of Barium Titanate, it has become the first choice for applications in Multilayer Ceramic Capacitors (MLCCs). The phase transitions of BaTiO<sub>3</sub> are as follows:



These phase transitions result in higher relative permittivity near the phase transition temperatures in  $\epsilon_r \sim T$  curve. For ferroelectric BaTiO<sub>3</sub>, when more than one kind of ions reside in

one of the available cation sub-lattices to form solid solution, then the normal sharp phase transition at  $T_C$  from ferroelectric to paraelectric state becomes diffused [2].

Recently Liu and Ren [2] reported that  $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  (BZT-BCT) possesses high permittivity around 3500 and low loss and it is a good ferroelectric material because of its high spontaneous polarization. It possesses morphotropic phase boundary emerging from tetragonal- rhombohedral phase coexistence. An MPB denotes an abrupt structural change with composition at constant temperature in a solid solution range. In the pseudo-binary ferroelectric system BZT-BCT it occurs close to the composition where BZT: BCT is 1:1 (molar). At composition near the MPB the relative permittivity, piezoelectric constant and the coupling coefficient shows peak and this feature can be exploited in commercial compositions.

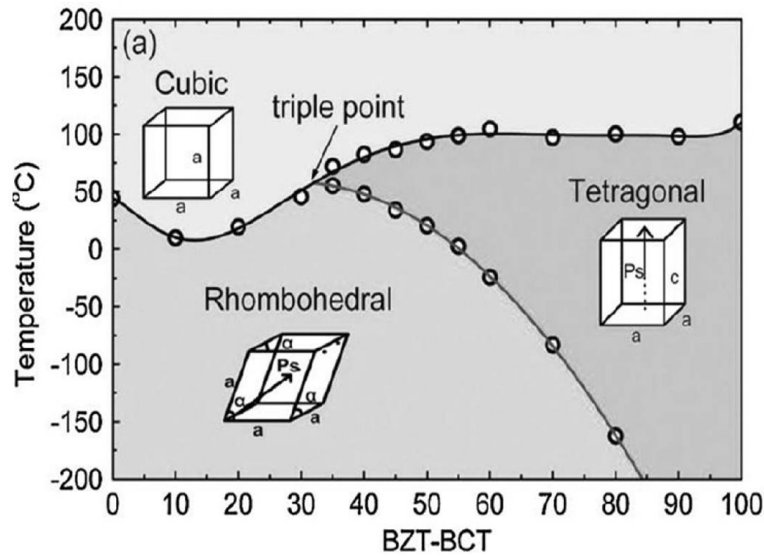


Fig 2: Phase diagram of pseudo-binary ferroelectric system  $\{x\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\}\text{-}\{(1-x)(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3\}$  [3]

- BZT-BCT has very high sintering temperature, more than 1400<sup>0</sup>C.
- It was observed from literature that glass additives can be used for sintering of barium titanate and modified barium titanate at low temperature and to get high permittivity, low loss and high energy density ceramics. The used glass should be alkali free and low loss.

# **Chapter 2**

## **Literature Survey**

Low temperature sintering of BaTiO<sub>3</sub> based composition:

**Vittayakorn *et.al.*** Investigated the densification and dielectric properties of bismuth doped barium titanate ceramics by conventional solid-state method. The doped samples are sintered 1350°C. XRD of the fabricated samples revealed only a monophasic perovskite. The properties like density, dielectric constant linearly increased with the sintering temperature. The maximum transition temperature was observed at 135°C with a relative permittivity at 1 KHz above the Curie temperature, the relative permittivity followed Curie-Weiss law [4].

**Wu *et al.*** studied the effect of Bi<sub>2</sub>O<sub>3</sub> on the microstructure and dielectric properties of BaTiO<sub>3</sub> based ceramic systems sintered at low temperatures. He reported that addition of small amounts of Bi<sub>2</sub>O<sub>3</sub> in BaTiO<sub>3</sub> reduced the sintering temperature from 1300<sup>0</sup>C to 1130<sup>0</sup>C and the bulk density increased with increasing Bi<sub>2</sub>O<sub>3</sub>. The dielectric constant increased up to 0.8 mol% Bi<sub>2</sub>O<sub>3</sub> additive while the dielectric loss decreased [5].

**Caballero *et al.*** stated that when ZnO is used as the dopant precursor in BaTiO<sub>3</sub>, ZnO redistribution takes place while heating by vapour-phase transport and grain boundary diffusion as no liquid phase formation takes place till 1400°C. Also the sintering is assumed to take place by solid-state diffusion due to the same reason of no detection of liquid till 1350°C. They have observed that the ZnO gets strongly segregated at the grain boundaries because of its very low solubility (less than several thousand ppm). They found out that density of materials doped with solid ZnO went as high as 99% for sintering temperatures 100°C lower than for undoped BaTiO<sub>3</sub>. Considering the electrical parameters, dielectric constants between 2000-3000 were measured for the ZnO-doped samples. Even the dielectric losses were well below 1% for all the ZnO-doped samples, even for samples with huge concentrations of dopants. All these properties

induced ZnO-doped BaTiO<sub>3</sub> to be used for high-quality capacitors and the heavily doped samples can be applied in the field of capacitor-varistor integration [6].

**X.Wang *et al.*** studied the effect of glass additive [27.68 BaCO<sub>3</sub>–6.92SrCO<sub>3</sub>–29 TiO<sub>2</sub>–22 SiO<sub>2</sub>–12 Al<sub>2</sub>O<sub>3</sub>–2.4 BaF<sub>2</sub> (mol%)] in barium titanate ceramics and its influence on electrical breakdown strength in relation with energy storage properties. Results shows that average grain size reduced with increasing glass concentration and also the dielectric constant decreased and the dielectric breakdown strength increased as glass concentration increased. It was also found that the energy storage density of the ceramics increased gradually with increasing glass concentration. The increase of the dielectric breakdown strength is attributed to the decrease of grain size and the improvement of charge transport behavior respectively. Moreover, as the glass concentration increases, the energy storage density of the ceramics increases gradually [7].

**Sreenivas Puli *et al.*** synthesized BaO-B<sub>2</sub>O<sub>3</sub>-ZnO- BZT–BCT glass ceramic composite for high energy density storage capacitors. X-ray diffraction and Raman spectroscopy studies of the sintered pellets revealed the pure perovskite phase with tetragonal structure. Pure ceramic BZT–BCT sample exhibits the well saturated hysteresis behaviour. Increase in the amount of glass composition with pure BZT–BCT, glass mixed ceramic P-E hysteresis loops becomes almost linear. As the glass wt% of the composition increased from 10-50%, the dielectric breakdown strength increased ~600 kV/cm and dielectric permittivity increased initially and then decreased for lateral compositions due to higher amount of glass. Higher breakdown strength and low loss might be due to the presence of alkali free glass and low loss dielectric BZT–BCT compositions [8].

**Zhang *et al.*** investigated the effect of Improved Energy Storage Density in Barium Strontium Titanate (BST) by Addition of BaO–SiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> Glass. They observed that breakdown strength is notably improved due to the decrease of the porosity and the reduction of the grain size and pore size in glass added samples. For the samples with addition of 5 vol% glass the energy density was increased by 2.4 times higher than that of pure BST. The improvement of energy density could be mainly attributed to the increase of the breakdown strength and the decrease of the remnant polarization [9].

**Young *et al.*** studied the effect of a BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub> glass additive on the breakdown strength of BaTiO<sub>3</sub> and found that the breakdown strength of the samples containing 20 vol. % glass was enhanced 2.8 time compared with that of pure Ba.TiO<sub>3</sub> [10].

**Prasad *et al.*** studied the effect of dielectric anomaly in strontium borate – bismuth vanadate glass nanocomposite. They observed that the nano-crystallization of bismuth vanadate were characterized for their structural, thermal and dielectric properties. The T<sub>g</sub> and T<sub>cr</sub> were determined using DTA. The dielectric constant and dielectric loss measurements were carried out on the as quenched and heat treated glass nanocomposite samples in the frequency range 100Hz-10MHZ. The x –ray structural and thermal characterization of both as quenched and heat treated samples confirmed the dissociation and reformation of Biv via the reaction through less energy favoured intermediate phases. Both the as-quenched and heat treated samples exhibits broad dielectric anomalies in the vicinity of the ferroelectric- paraelectric transition temperature of parent bismuth vanadate crystalline phases [11].

**Mao *et al.*** studied the effect of preparation and dielectric properties of Nb<sub>2</sub>O<sub>5</sub>-BaO-Na<sub>2</sub>O- SiO<sub>2</sub> glass – ceramic for energy storage capacitors. He observed that glass ceramics with lead content are still the most common used materials due to their high Curie point and dielectric constant.

However, because of the high temperature during the melting of glass ceramic mixture, mostly above  $1400^{\circ}\text{C}$ , the volatilization of Pb would be harmful to human health. Since energy storage density of the materials is proportional to dielectric constant and square of breakdown strength. Dielectric constant increases with crystallization temperature, and the difference of the dielectric constant is less than 10% at the frequency range from 100HZ to 100KHZ. Dielectric constant of the materials crystallized at  $750^{\circ}\text{C}$  and  $800^{\circ}\text{C}$  has negative linear relationship at the temperature range from  $-40^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , which is contrary to the material crystallized at  $900^{\circ}\text{C}$  [12].

**Jun Du *et al.*** studied the effect of preparation and characterization of dielectric glass – ceramics in  $\text{Na}_2\text{O} - \text{PbO}-\text{Nb}_2\text{O}_5-\text{SiO}_2$  system. The dielectric properties of the glass ceramics formed through controlled crystallizations have strong dependence on the phase assemblages that developed during heat treatment.

The dielectric constants were found in samples annealed at  $850^{\circ}\text{C}$  for 3 hours. Microstructure observation shows that randomly oriented nanometre size crystalline are found with residual glass concentrated at crystallite boundaries. It has been found that dielectric constant of glass ceramic can be tailored through controlling the nature of crystallite phases. The glass ceramic annealed at  $850^{\circ}\text{C}$  for 3 hours display the best dielectric performance which is attributed to the presence of  $\text{NaNbO}_3\text{-PbNbO}_6$  solid solution [13].

**Shankar *et al.*** studied the effect of crystallization dielectric and optical studies on strontium tetra borate glasses containing bismuth titanate. The dielectric constant of glass samples was found to increase with increase in  $\text{Bi}_2\text{O}_3.\text{TiO}_2$  content, and the dielectric loss ( $\tan\delta$ ) values were reasonably low (0.02 to 0.04) for all the compositions under study, in the 100Hz to 100 KHz frequency range. The frequency response of  $\epsilon_r$  and the dielectric loss of crystallite sample



exhibited sharp piezoelectrically induced resonance in the 185 to 200 KHz range. The resonance peak was found to shift towards lower frequencies with increasing temperature and higher frequency with increasing pressure. However the sharp piezoelectric resonances exhibited by the present glass ceramics in the 185-200 KHz frequency range suggest that there is scope for exploitation of these materials for piezo-resonant electro-optic modulator applications [14].

## 2.1 OBJECTIVE

The objective of the present work is to study the two different alkali free low melting glass additive on densification and dielectric properties of BZT-BCT ceramics. The two different glass additives are strontium borate ( $\text{SrB}_4\text{O}_7$ ) and  $\text{BaO} \cdot \text{SiO}_2 \cdot \text{B}_2\text{O}_3$ . The above mentioned objective can be fulfilled by using following steps:

1. Synthesis of phase pure  $\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3$  -  $(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$  [BZT-50BCT] by conventional solid – state reaction route.
2. Preparation of strontium borate ( $\text{SrB}_4\text{O}_7$ ) and  $\text{BaO} \cdot \text{SiO}_2 \cdot \text{B}_2\text{O}_3$  glass by melt quenching method.
3. To study the densification behavior of BZT-50BCT using glass additives.
4. To study the phase present in sintered BZT-50BCT samples.
5. To study the dielectric property of sintered samples.
6. To study the microstructure of the sintered ceramics.

# **Chapter 3**

## **Experimental work**

### 3.1 Preparation of BZT-BCT powders

Barium calcium zirconate titanate [ $x \text{ Ba} (\text{Zr}_{0.1}\text{Ti}_{0.9}) \text{O}_3 - (1-x)(\text{Ba}_{0.85}\text{Ca}_{0.15}) \text{TiO}_3$  (BZT-BCT)] ( $x=0.5$ ) ceramics was synthesized by solid state method. Reagent grade;  $\text{BaCO}_3$  (99%),  $\text{CaCO}_3$  (99%) and  $\text{ZrO}_2$  (99.9%),  $\text{TiO}_2$  (99.9%) were used as the starting material. All the compounds were stoichiometrically weighed and milled for 10h, using planetary milling with zirconia ball and isopropyl alcohol media. The calcination was performed at  $1200^\circ\text{C}$  in an alumina crucible.

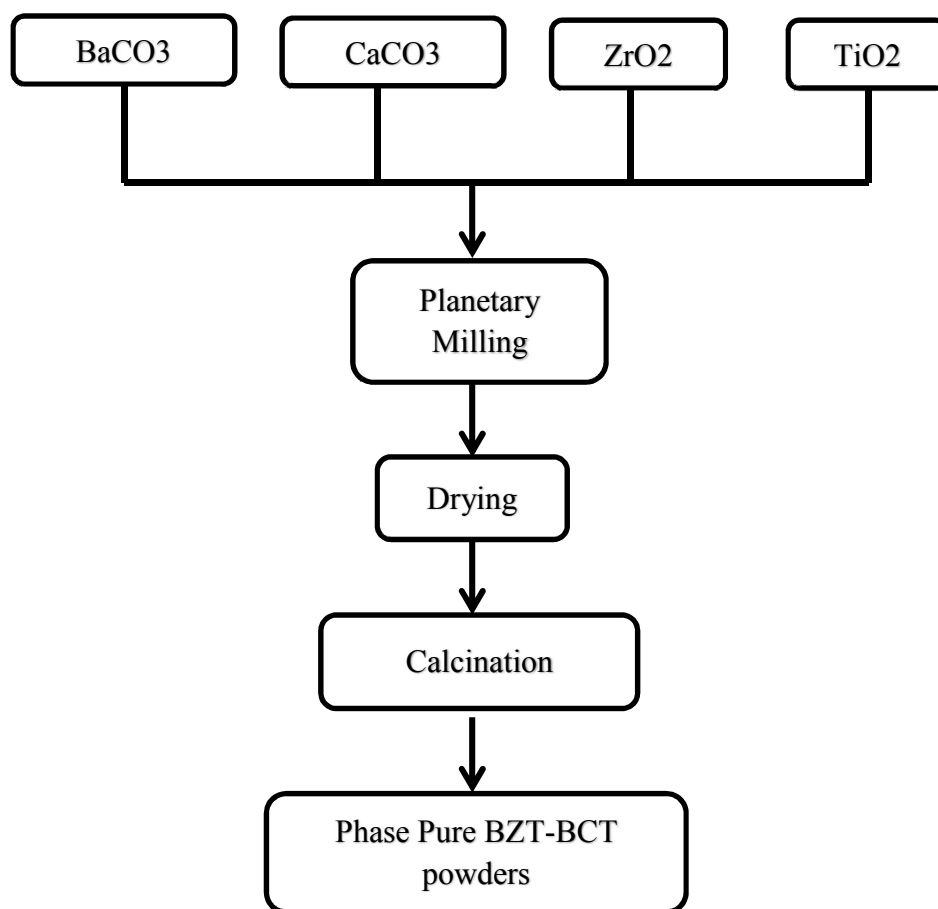


Fig 3: Flow chart for Preparation of BZT-BCT powders

### 3.2 Preparation of $\text{SrB}_4\text{O}_7$ glass

The raw material of this glass is  $\text{SrCO}_3$  and  $\text{H}_3\text{BO}_3$ . The stoichiometric powders were mixed for 6 h in alcohol medium using zirconia balls. The dried powders were then melted in a platinum crucible at  $1150^\circ\text{C}$  for 1 h. The molten glass was quenched in water and then planetary milled for 8h to get a fine powder.

Calculated amount of  $\text{SrB}_4\text{O}_7$  was added to the BZT-BCT powder so that during sintering it can produce dense ceramic. The amount of glass powder added to BZT-BCT was 10, 20, 30, 50 wt. % respectively. This mixture was pot milled for 6 h and then dried. After drying, the powder was taken out. Finally this was mixed with few drops of 5 wt. % PVA solution and uniaxially pressed into pellets at 4 ton and 90 sec dwelling time. Then pellets were sintered at  $900^\circ\text{C}$ ,  $1000^\circ\text{C}$ ,  $1050^\circ\text{C}$ ,  $1100^\circ\text{C}$  for different soaking period 15 minutes, 30 minutes, 1 hour, 2 hours and 4 hours taken for further characterization. Fig 4 and 5 describes the steps for powder preparation and sintering.

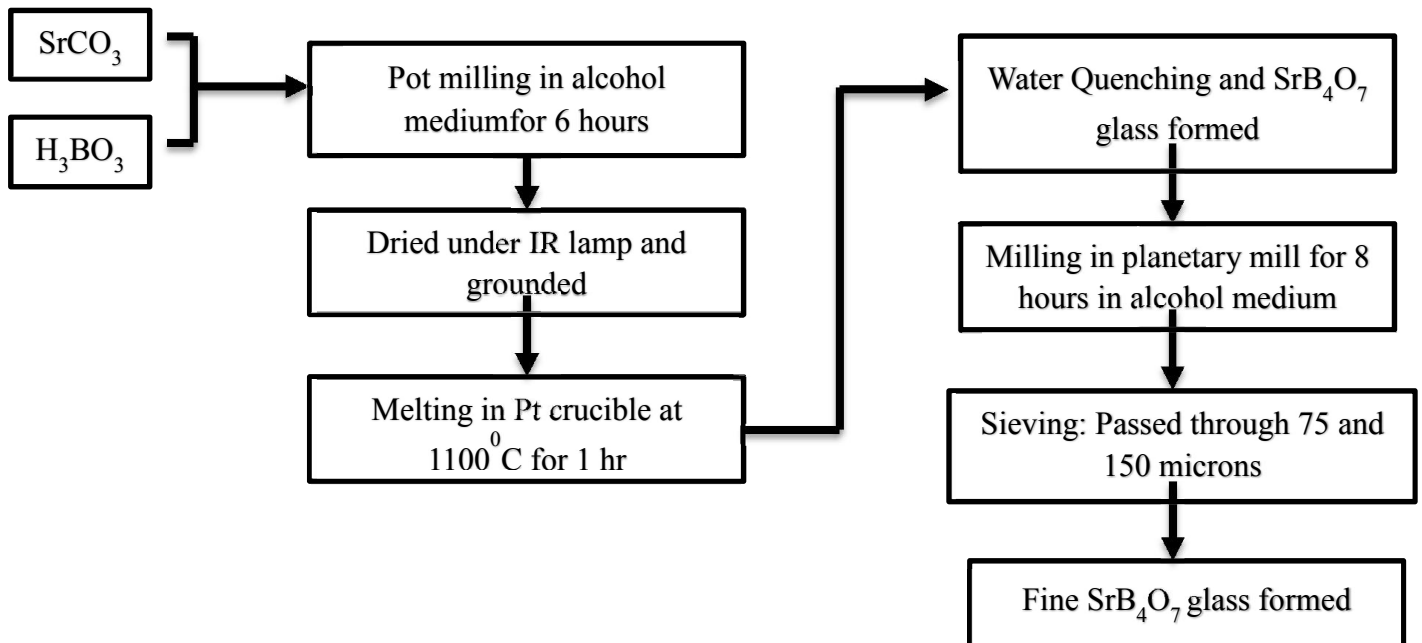


Fig 4: Flow Chart for the preparation of  $\text{SrB}_4\text{O}_7$  glass powder

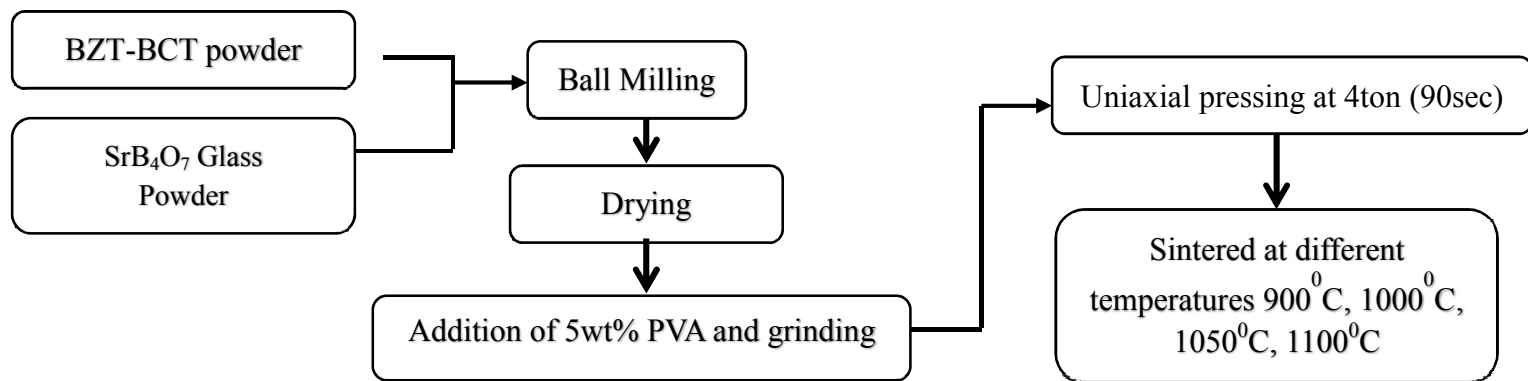


Fig 5: Flow Chart for the preparation of  $\text{SrB}_4\text{O}_7$  glass added BZT-BCT ceramic

### 3.3 Preparation of $\text{BaO} \cdot \text{SiO}_2 \cdot \text{B}_2\text{O}_3$ Glass

The composition of the glass is 48.4%  $\text{BaO}$ –20.3%  $\text{SiO}_2$ –26.7%  $\text{B}_2\text{O}_3$ –0.7%  $\text{Al}_2\text{O}_3$ –1.95%  $\text{ZrO}_2$ –1.94%  $\text{SrO}$  (mol%). The stoichiometric powders were mixed for 6 h in alcohol medium using zirconia balls. The dried powders were then melted in an  $\text{Al}_2\text{O}_3$  crucible at  $1150^\circ\text{C}$  for 2 h. The molten glass was quenched in water and then planetary milled for 8 h to get a fine powder.

Calculated amount of  $\text{BaO} \cdot \text{SiO}_2 \cdot \text{B}_2\text{O}_3$  was added to the BZT-BCT powder so that during sintering it can produce  $\text{BaO} \cdot \text{SiO}_2 \cdot \text{B}_2\text{O}_3$  glass ceramic composite. The amount of glass powder added to BZT-BCT was 5, 10, 20 wt. % respectively. This mixture was pot milled for 6 h and then dried. After drying, the powder was taken out. Finally this was mixed with few drops of 5 wt. % PVA solution and uniaxially pressed into pellets at 4 ton and 90 sec dwelling time. Then pellets were sintered at  $1100^\circ\text{C}$ ,  $1150^\circ\text{C}$  for different soaking period 1 and 2 h and taken for further characterization. Fig 5 and 6 describes the steps for powder preparation and sintering.

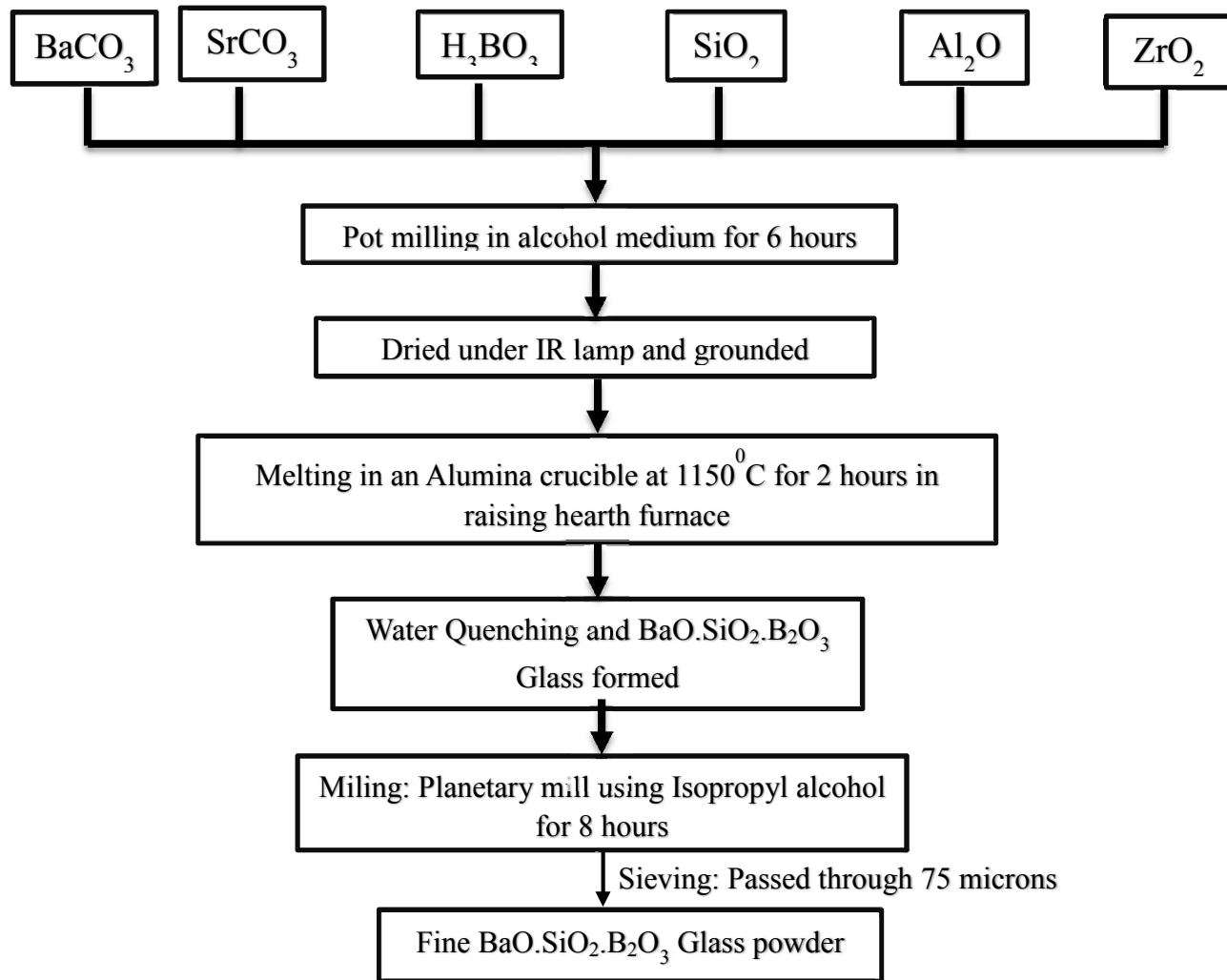


Fig 6: Flow Chart for the preparation of BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub> glass powder

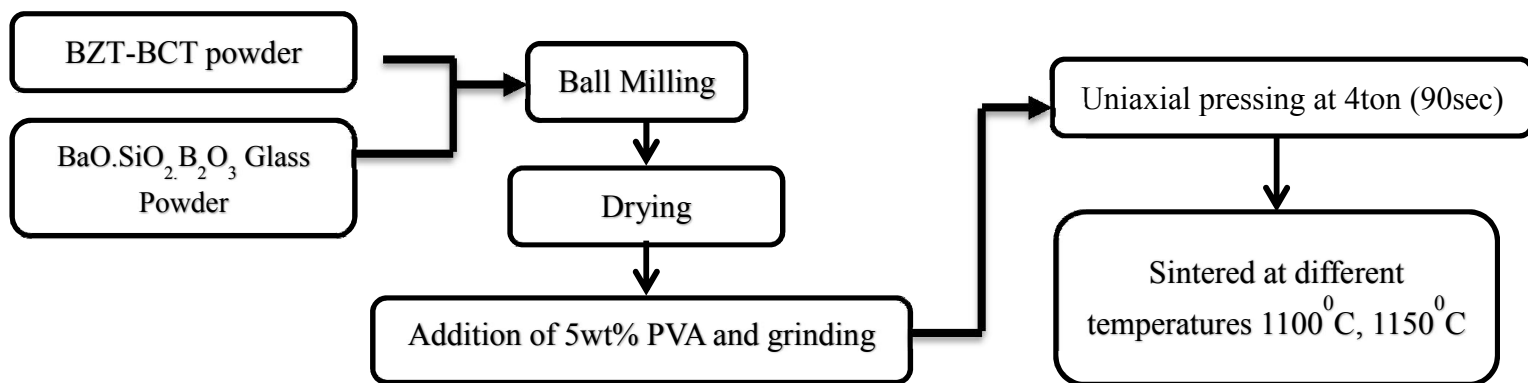


Fig 7: Flow Chart for the preparation of BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub> glass added BZT-BCT Ceramic

### **3.4 Characterization**

#### **3.4.1 Phase and microstructure analysis**

The phase evolution of the glass powder and sintered pellets were characterized by X- Ray Diffraction Technique (Rigaku, Japan). Scanning of samples was done between  $2\theta$  ranges 15 to  $80^\circ$  range in continuous scan mode with 20 deg/sec scan rate. Phases present in the samples was identified by the search-match facility available with Philips X`Pert High Score Software.

Samples were polished and ultrasonicated with acetone to remove the powder debris from the surface. Microstructural and compositional analysis was done using FESEM (Field Emission Scanning Electron Microscope, Nova Nano SEM/FEI).

#### **3.4.2 Density Measurement:**

The Bulk density of the sintered pellets was calculated using the formula,

$$\text{B.D.} = \frac{\text{Dry Weight}}{\text{Soaked Weight} - \text{Suspended Weight}}$$

Bulk density study of the sintered samples were done by Archimedes principle, using vacuum method in Kerosene medium (sp, gr. 0.81715).

#### **3.4.3 Dielectric Measurement:**

For dielectric measurement, samples were polished and then ultrasonicated using acetone to wash away the fine debris on the pellet surface.

The clean samples were electroded with silver paste followed by curing at  $550^\circ\text{C}$  for 30min. Dielectric measurement was carried out using HIOKI LCR (3532-50) meter in frequency range of 42 Hz to 1MHz.



# **Chapter 4**

## **Results and Discussion**

#### **4.1 Densification of BZT-BCT with $\text{SrB}_4\text{O}_7$ glass:**

From table 1 it was observed that at low concentration (10, 20 wt %) of glass and at low sintering temperature (900°C) BZT-BCT could not be sintered. But with increase in sintering temperature densification improves but it was only 70% of the true density of BZT-BCT (5.78 gm/cc). With higher concentration of glass also (30, 50 wt %) pellets could not be sintered. It is known that in liquid phase sintering the process of particle rearrangement and densification depends on many parameters like the surface free energy of the liquid–vapor interface, viscosity of the liquid, contact angle, and diameter of the capillary [15]. In the present case, nonwetting nature of the molten glass or very low viscosity of the glass may be reason for poor densification of the samples.

**Table 1**Density of  $\text{SrB}_4\text{O}_7$  added BZT-BCT glass ceramics

<b>Glass concentration</b>	<b>Sintering Temperature and Time</b>	<b>Geometrical Density (gm/cc)</b>	<b>Physical Appearance</b>
10 Wt. %	900 <sup>0</sup> C – 4 hrs.	3.85	Poor densification
20 Wt. %	900 <sup>0</sup> C – 4 hrs.	3.78	Poor densification
10 Wt. %	1000 <sup>0</sup> C – 4 hrs.	4.37	Glass melted and small amount of glass expelled out but pellet did not stuck to the alumina substrate.
10 Wt. %	1050 <sup>0</sup> C- 30 minutes	3.56	Glass melted and small amount of glass expelled out but pellet did not stuck to the alumina substrate.
20 Wt. %	1050 <sup>0</sup> C- 30 minutes	4.15	. Glass melted and small amount of glass expelled out but pellet did not stuck to the alumina substrate.
30 Wt. % & 50 Wt. %	1100 <sup>0</sup> C - 4 hrs.	-	Glass melted and small amount of glass expelled out and density of the pellets could not be measured.
30 Wt. %	1000 <sup>0</sup> C-2 hrs.	3.8	Poor densification
50 Wt. %	1000 <sup>0</sup> C-2hrs	3.6	Poor densification
30 Wt. % & 50 Wt. %	1100 <sup>0</sup> C- 15 minutes	-	Glass got melted heavily and pellets stuck to the alumina substrate.
30 Wt. % & 50 Wt. %	1050 <sup>0</sup> C- 2 hrs.	-	Glass got melted heavily and pellets stuck to the alumina substrate.

## 4.2 XRD analysis of $\text{SrB}_4\text{O}_7$ glass

Fig.8 shows the XRD pattern of  $\text{SrB}_4\text{O}_7$  glass, it is a signature of glass sample. Fig. 9 shows the XRD patterns of  $\text{SrB}_4\text{O}_7$  glass (30 and 50 wt %) added BZT-BCT sintered at  $1000^\circ\text{C}$ . Perovskite phase was observed with small amount impurity phase.

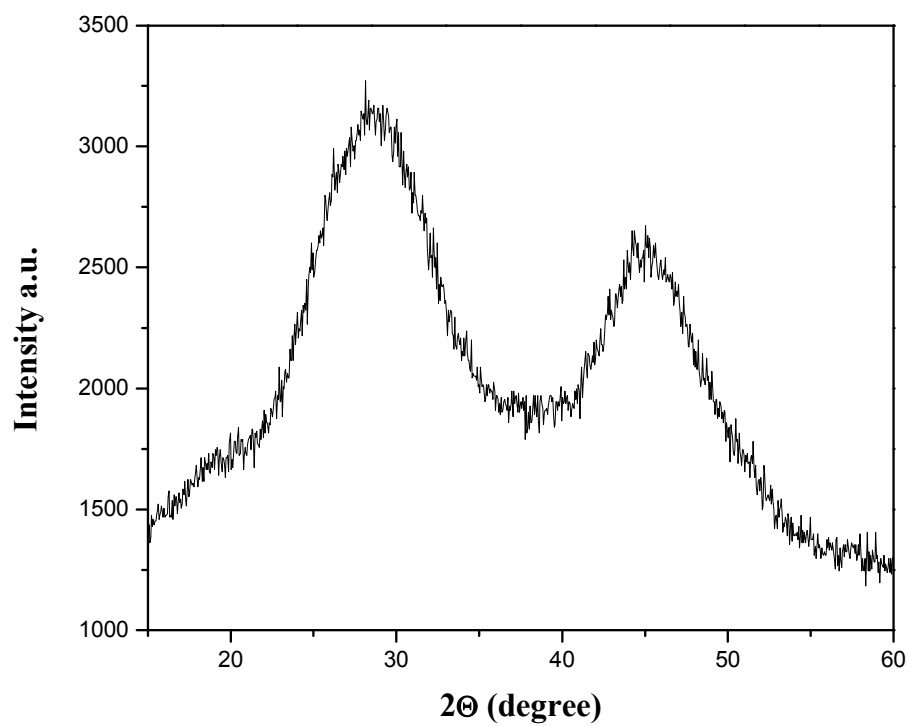


Fig 8: XRD pattern of  $\text{SrB}_4\text{O}_7$  glass

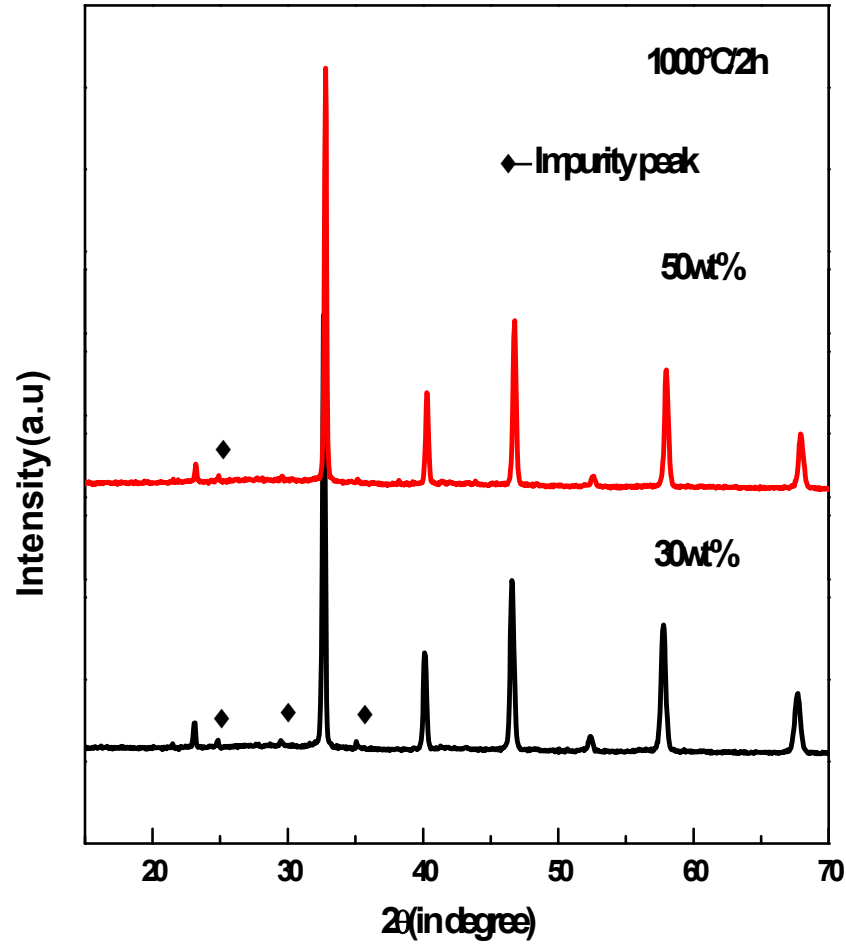


Fig 9: X-ray diffraction patterns of the  $\text{SrB}_4\text{O}_7$  added BZT-BCT ceramics sintered at  $1000^\circ\text{C}/2\text{h}$ .

#### 4.3 Bulk Density of modified BZT-BCT glass ceramics.

Table 2 and Fig.10 shows the bulk density of BZT-BCT for different sintering temperature and time. The bulk density of BZT-BCT increases with increase in glass concentration. For  $1100^\circ\text{C}$  sintered sample with increase in soaking time density increases. Highest density was achieved in  $1150^\circ\text{C}$  sintered sample for higher concentration of glass addition.

The addition of the glass not only improves the relative density of sintered BZT-BCT ceramics but also decreases the sintering temperature of BZT-BCT usually it is more than 1400°C. For BZT-BCT system BaO, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> is a effective sintering aid and 94% of theoretical density could be achieved at 1100°C.

**Table 2**

Bulk Density of BaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass added BZT-BCT ceramics

<b>Compositions</b>	<b>Sintering Temperature</b>	<b>Soaking Time (hr)</b>	<b>Bulk Density (gm/cc)</b>
<b>5wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1100 <sup>0</sup> C	1	4.8
<b>10wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1100 <sup>0</sup> C	1	5.01
<b>20wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1100 <sup>0</sup> C	1	5.33
<b>5wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1100 <sup>0</sup> C	2	5.11
<b>10wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1100 <sup>0</sup> C	2	5.12
<b>20wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1100 <sup>0</sup> C	2	5.37
<b>5wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1150 <sup>0</sup> C	1	5.2
<b>10wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1150 <sup>0</sup> C	1	5.33
<b>20wt % BaO.SiO<sub>2</sub>.B<sub>2</sub>O<sub>3</sub></b>	1150 <sup>0</sup> C	1	5.53

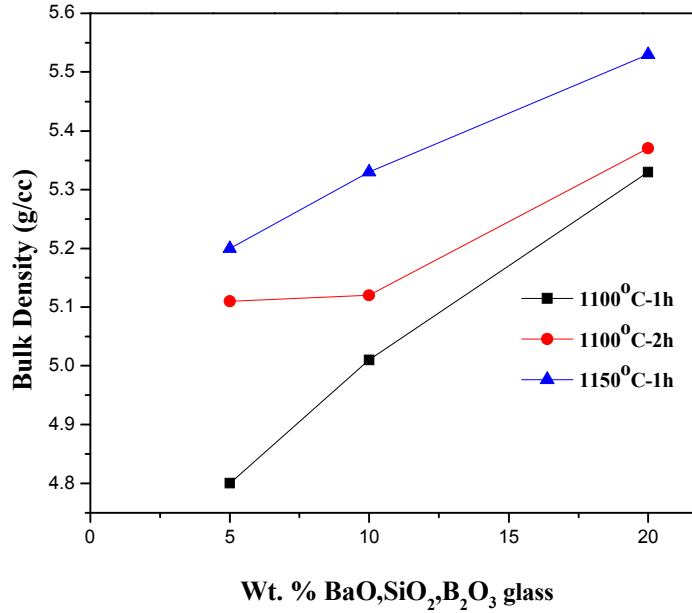


Fig 10: Bulk Density of BaO, SiO<sub>2</sub>, and B<sub>2</sub>O<sub>3</sub> glass added BZT-BCT ceramics.

#### 4.4 Phase analysis of BaO, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> glass and glass added sintered BZT-BCT ceramics:

Fig.11 shows the XRD pattern of glass sample. Fig.12 (a) & (b) shows the X-ray diffraction patterns of the modified BZT-BCT glass ceramics sintered at 1100°C/2h and 1150°C/1h, respectively. It can be observed that pure perovskite phase retained in the sintered pellet but a small amount of CaTiO<sub>3</sub> impurity phase also generated. The modified BZT-BCT glass ceramic possessed tetragonal crystal structure and it was matched with JCPDS card no 80-2213. Moreover, it is clear that the position of diffraction peaks of the modified glass ceramics has shifted to lower angle with increase in glass content. It may be due to small amount of glass composition have diffused into the BZT-BCT lattice side to form a solid solution.

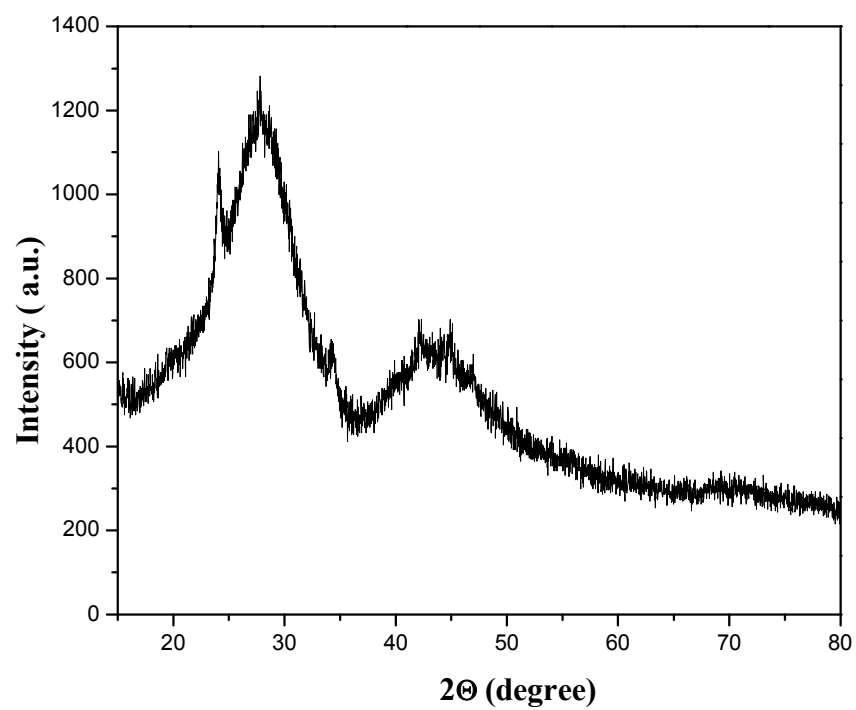


Fig 11: XRD analysis of BaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass



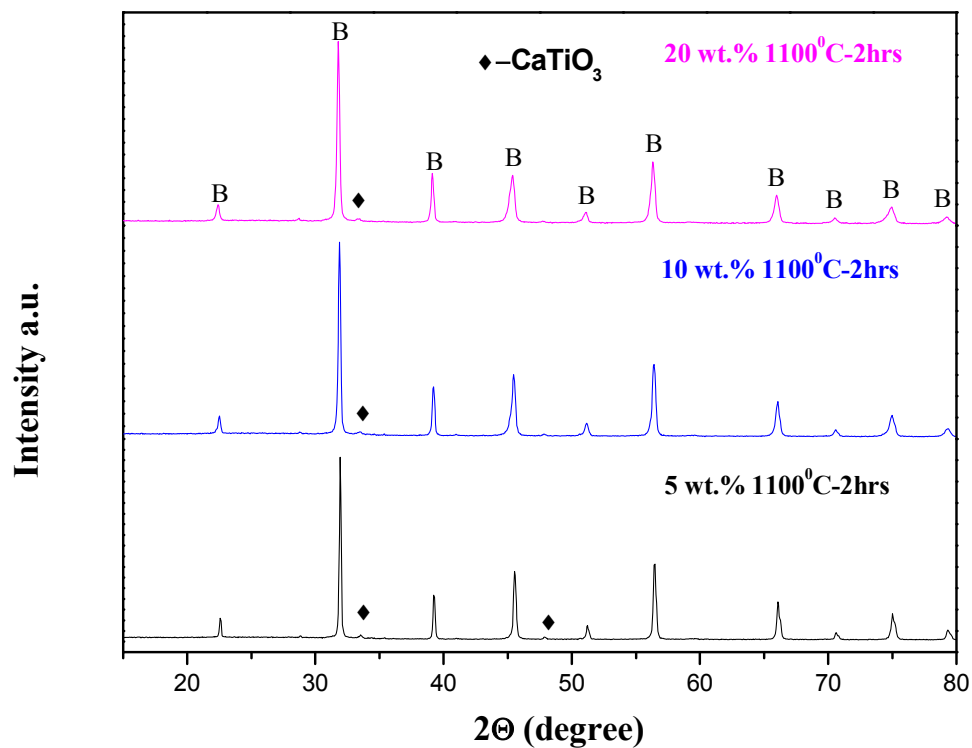


Fig 12 (a): X-ray diffraction patterns of the glass added BZT-BCT ceramics sintered at 1100°C for 2h

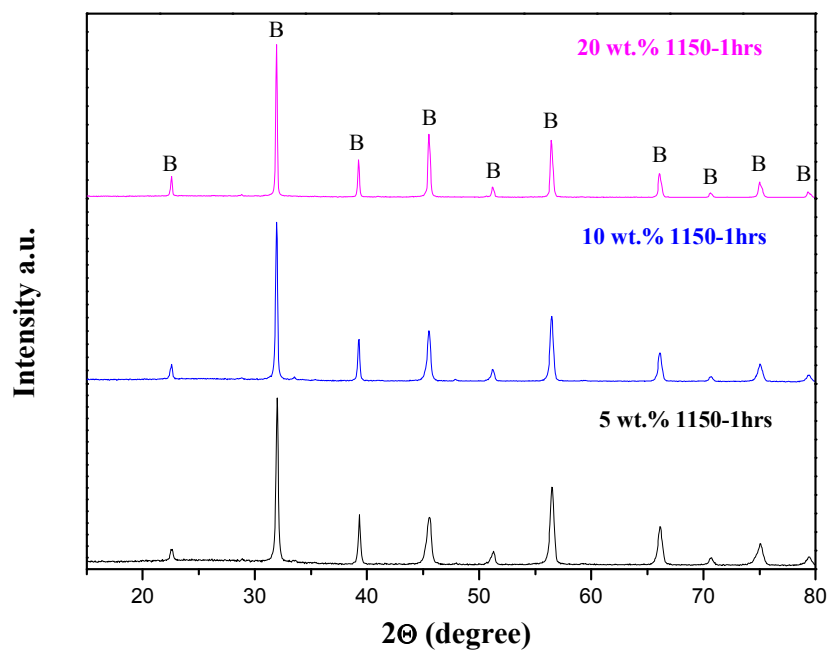


Fig 12 (b): X-ray diffraction patterns of the glass added BZT-BCT ceramics sintered at 1150°C for 1hrs

## 4.5 Dielectric Properties

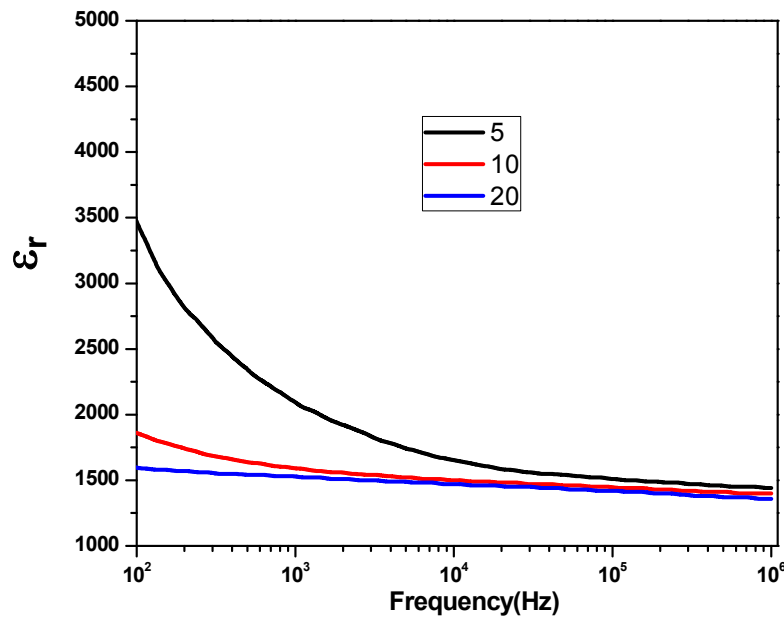


Fig 13(a): Room temperature relative permittivity ( $\epsilon_r$ ) of glass added BZT-BCT ceramics sintered at 1100°C for 2 hrs.

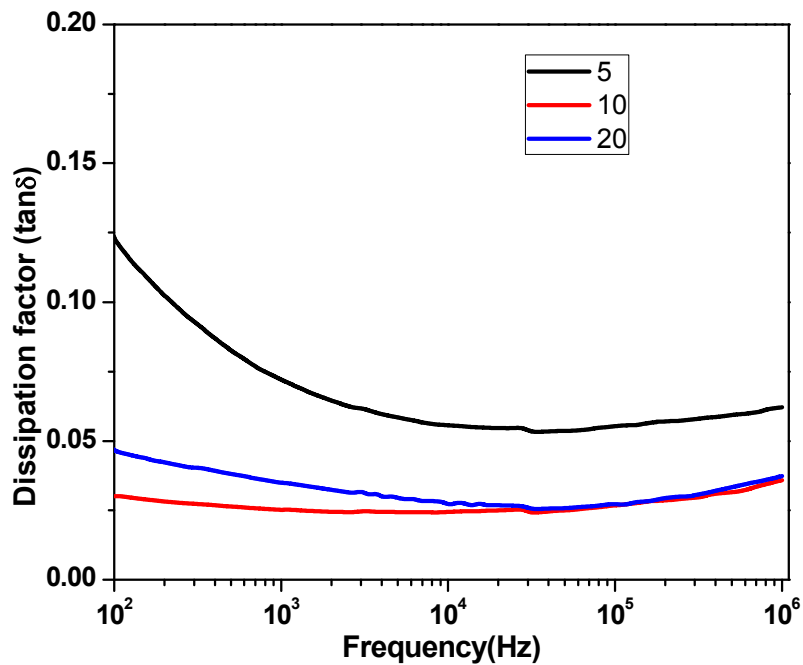


Fig 13 (b): Room temperature dissipation factor ( $\tan\delta$ ) of glass added BZT-BCT ceramics sintered at 1100°C for 2 hrs.

The frequency dependence of the relative permittivity and dissipation factor of BZT-BCT ceramics with different weight percent of BaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass are shown in Fig. 13 (a) & (b). 5 wt% glass added samples have higher permittivity with higher loss. Low frequency dispersion below 1 KHz could be attributed to space charge polarization in the samples. With high amount of glass addition, permittivity and tan $\delta$  both decreases. Frequency dispersion is reduced significantly that may be due to presence of insulating glassy phase around grain boundary. It is to be mentioned that there are no significant change in dielectric property was observed for 1150°C [Fig. 14 (a) & (b)] sintered sample.

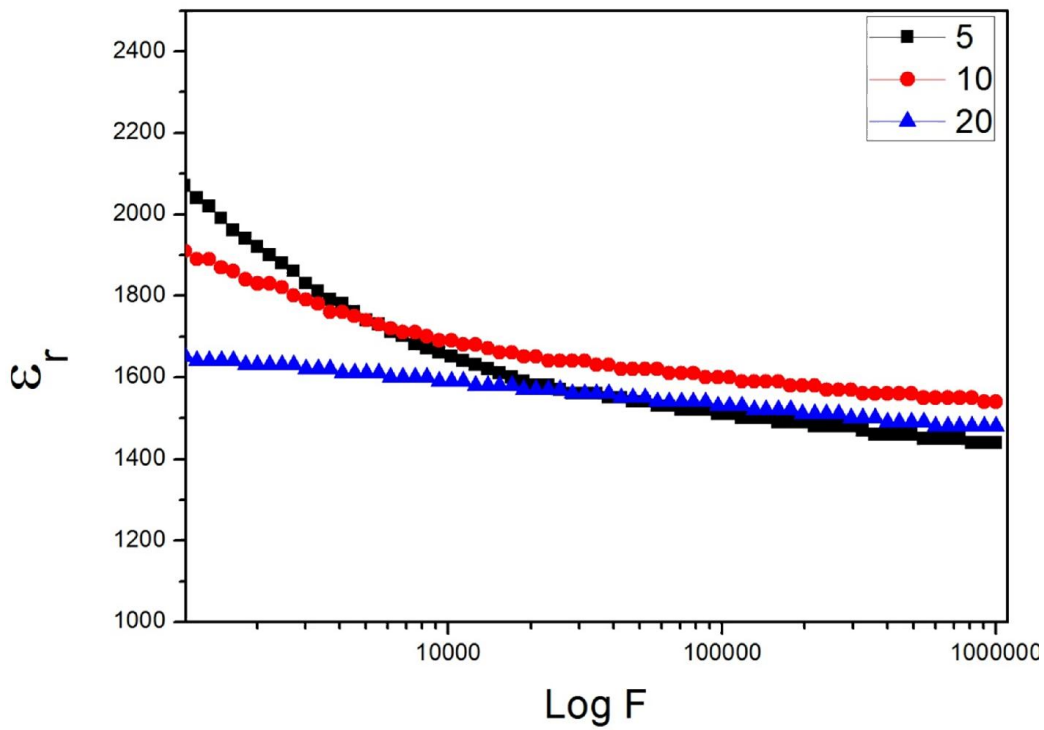


Fig 14 (a): Room temperature relative permittivity ( $\epsilon_r$ ) of glass added BZT-BCT ceramics sintered at 1150°C for 1 hrs.

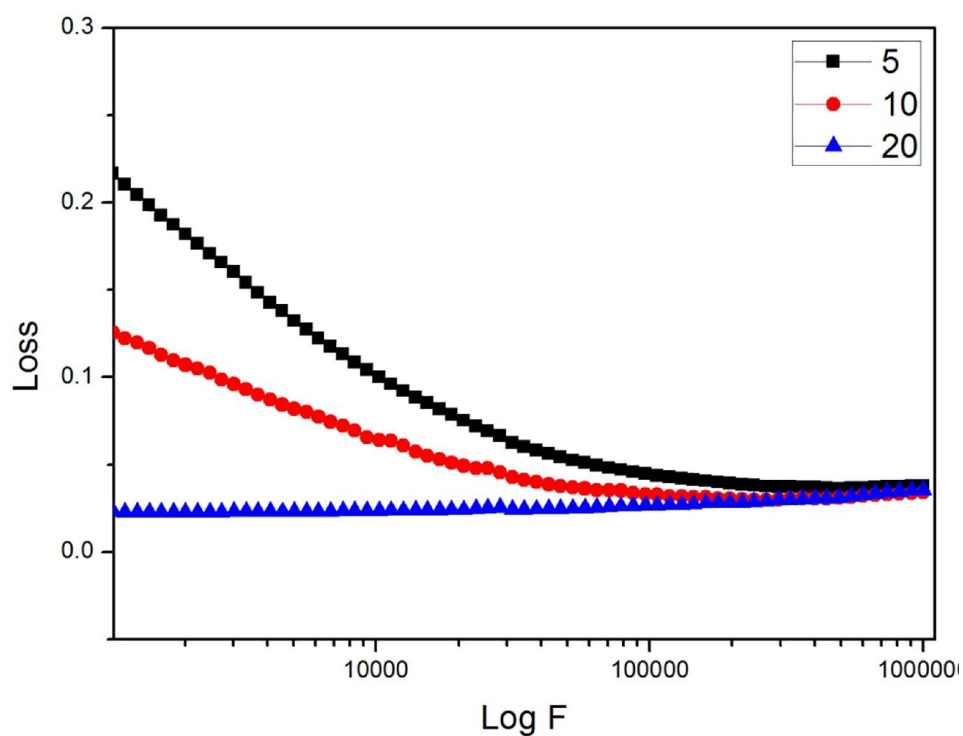
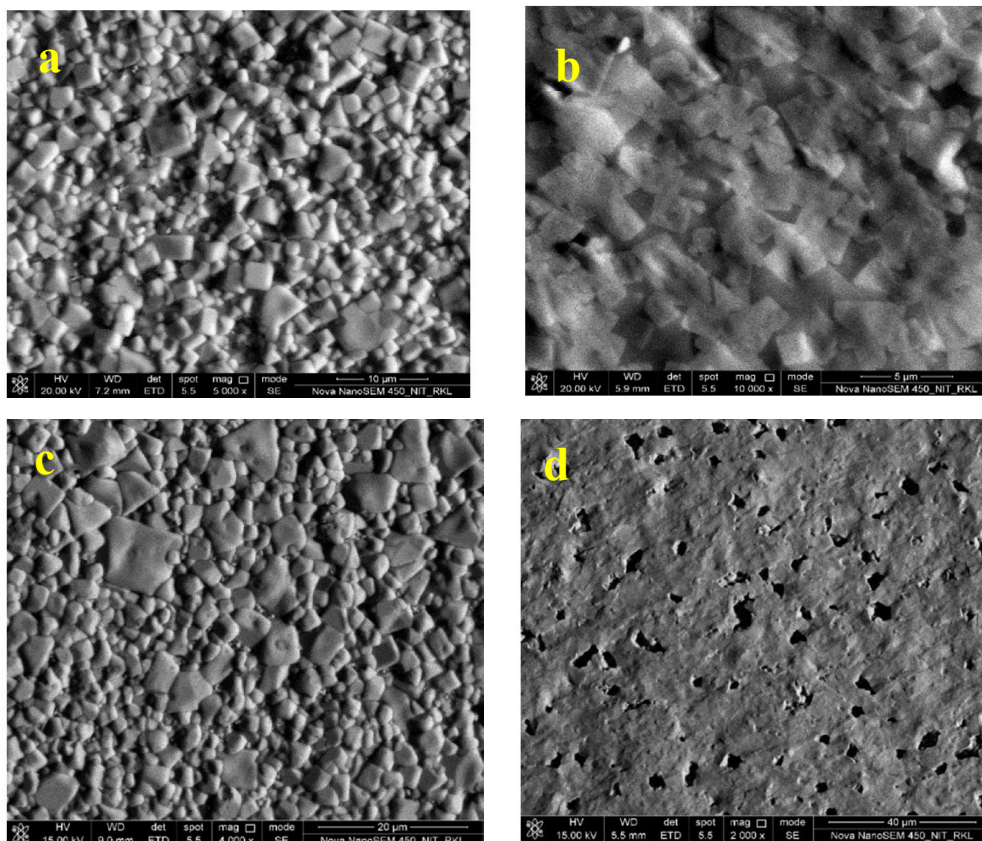
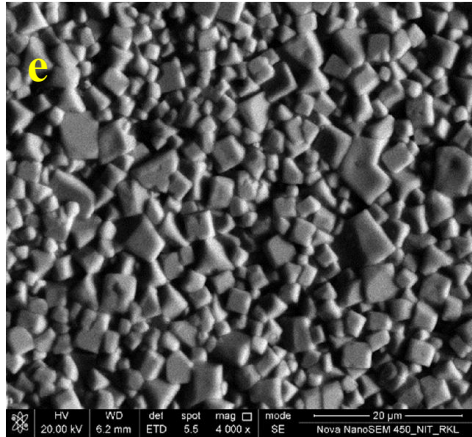


Fig 14(b): Room temperature dissipation factor ( $\tan\delta$ ) of glass added BZT-BCT ceramics sintered at 1150<sup>0</sup>C for 1 hrs.

#### 4.6 Microstructural Analysis





Temperature	Average Grain size( $\mu\text{m}$ )
1100°C/1h	1.7 (0.9-3.6)
1100°C/2h	1.91(1.3-3.3)
1150°C/1h	1.95(1.3-3.6)

Fig 15: FESEM micrograph of as fired surface and fracture of 10 wt% BaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> added BZT-BCT ceramics (a) -(b) 1100°C/1h (c)-(d) 1100°C/2h (e) 1150°C/1h

Fig 15 shows the FESEM micrograph of the as fired surface and fracture surface of BZT-BCT sintered with 10 wt% BaO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass additives. The grain size of the sintered body increases marginally with increase in sintering temperature and time. The glass additive promotes exaggerated grain growth as observed from the microstructure. Fracture surface shows intergranular fracture in the sample and porosity.

# **Chapter 5**

## **Conclusion and References**

## 5.1 Conclusions

- $\text{SrB}_4\text{O}_7$  glass is not an effective additive for sintering of BZT-BCT.
- $\text{BaO}.\text{SiO}_2.\text{B}_2\text{O}_3$  glass is useful for sintering of BZT-BCT at around  $1150^\circ\text{C}$ .
- Higher glass content (around 20 %) improves the density but it degrades the dielectric property.
- 10 wt. % glass content is effective to get a reasonable density and good dielectric property.
- Addition of glass promotes exaggerated grain growth.

## 5.2 References

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